UNIVERSITY OF TECHNOLOGY SYDNEY

Enhancement of the UV Emission in Metal Nanoparticle-Coated ZnO

by
Saskia FIEDLER

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Declaration of Original Authorship

I, Saskia FIEDLER, declare that this thesis titled, "Enhancement of the UV Emission in Metal Nanoparticle-Coated ZnO ", is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Mathematical and Physical Sciences, Faculty of Science at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise reference or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis. This document has not been submitted for qualifications at any other academic institution.

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Abstract

Large emission enhancement factors resulting from orders of magnitude increases in ultra-violet (UV) luminescence in ZnO have been reported, due to the presence of a surface coating of either Au or Al nanoparticles. Two significantly different models have been proposed to explain the observed increase in the UV light output. One involving the decay of metal nanoparticles localised surface plasmons (LSP) into hot carriers and their radiative recombination following injection into the ZnO conduction and valence bands. The other describes the creation of an additional fast relaxation pathway via a dipole-dipole coupling mechanism between excitons in ZnO and the metal nanoparticle LSPs, resulting in an improved ZnO UV spontaneous emission rate. This work specifically addresses this significant discrepancy in the existing literature, that reports metal nanoparticle-induced light emission in ZnO.

The UV emission enhancement mechanism between *a*-plane ZnO single crystals and ZnO nanorods coated with Al and Au nanoparticles were systemically investigated in this thesis, using cathodoluminescence (CL) and photoluminescence (PL) spectroscopy in conjunction with ellipsometry, optical absorption and synchrotron valence band spectroscopy measurements. Significantly novel concurrent CL-PL techniques were also employed in this study. The presence of both metal surface films was found to enhance the ZnO UV emission. Moreover, changes to the surface band bending induced by the metal coating was confirmed and their effect on visible deep level (DL) defect related ZnO emission and surface electronic properties was considered.

For 5 nm-Au nanoparticle-coated ZnO nanorods, an up to 3.8-fold enhanced UV emission with no change in the intensity of the visible defect luminescence due to deep level recombination: quenching of the DL is hallmark characteristic of the hot carrier model. The underlying UV enhancement effect was found to be excitation depth-dependent with the largest enhancement being observed with light generation at the surface, closest to the ZnO-Au interface. Concurrent CL-PL showed that UV emission of the Au nanoparticle-coated ZnO samples under simultaneous electron beam and laser irradiation is identical to the electron beam excitation alone, confirming that while LSPs are created in the Au nanoparticles, hot electrons are not injected into the conduction band of the ZnO. Furthermore, time-resolved PL measurements at 10 K revealed that the presence of the Au nanoparticle surface coating on ZnO nanorods produced a 40 ps reduced lifetime compared with the uncoated side of the sample. The corresponding Purcell enhancement

factor of only 1.4 is much lower than the observed UV enhancement of up to 3.8, indicating that the LSP-exciton coupling is not the cause of the UV enhancement. The findings collectively confirm that that neither of the two reported models can be responsible for the observed UV enhancement in these samples. Consequently an alternate mechanism is proposed which is consistent with all of the experimental results. This model suggests that the interband transitions in Au in the UV spectral range, from the 5d band to the partly filled 6sp conduction band, can be excited by the exciton emissions in ZnO via a resonance energy transfer mechanism. The creation of this additional, faster relaxation channel increases the exciton spontaneous emission rate, enhancing the observed UV emission of Au nanoparticle-coated ZnO.

In the case of the Al-coating, *a*-plane ZnO single crystals and ZnO nanorods were coated with a 2 nm thin Al film, resulting in an up to 12-fold enhancement of the UV PL emission. The increase was attributed to a strong Al LSP-exciton coupling mechanism. Additionally, below 80 K, the in-diffusion of the Al into the ZnO was found to contribute to measured increase in the total UV emission by increasing the Al I_6 bound exciton luminescence. The maximum UV enhancement was found at 80 K, where the bound excitons (BX) in ZnO are mostly thermally dissociated and the luminescence spectra are dominated by the free exciton (FX) emission. The LO-phonon replicas of the FX were also highly-enhanced by the Al-coating, indicating that the LSPs in the Al nanoparticles couple more favourably to the FX in the ZnO than to the BX. It was also found that the LSP-coupling to one of the three A, B and C FXs in ZnO is dependent on the ZnO crystal orientation and thereby the polarisation of the FX in ZnO with respect to the incident laser light. Furthermore, the strength of the LSP-exciton coupling was found to be dependent on the carrier density of ZnO with samples having higher carrier densities exhibiting a greater UV enhancement.

In conclusion, ZnO planar and nanorod samples coated with both Au and Al nanoparticles thin films in this work resulted in a large UV enhancement, arising from two different processes. The UV enhancement of the Au nanoparticle-coated ZnO samples was attributed to interband transitions in the Au nanoparticles, while the origin of the UV enhancement of the Al-coated ZnO samples was assigned to LSP-exciton coupling to preferably the FX in ZnO. The results of this thesis provide insight into why different explanations for the observed metal nanoparticle-induced emission enhancement in ZnO exist in the literature and why comprehensive characterisation of the structural and physical properties of both the ZnO and the metal nanoparticle ZnO composite is essential to establish the exact identity of the primary enhancement mechanism.

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List of Publications

S. Fiedler, L. O. Lee Cheong Lem, C. Ton-That and M. R. Phillips. "Mechanism behind enhanced UV emission of metal nanoparticle-coated ZnO ", E-MRS Fall 2018

S. Fiedler, L. O. Lee Cheong Lem, C. Ton-That and M. R. Phillips. "Investigation of Plasmonic UV Emission Enhancement from Au-coated ZnO Nanorods", ICONN 2018

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A. M. Berhane, K. -Y. Jeong, Z. Bodrog, S. Fiedler, T. Schröder, N. V. Triviño, T. Palacios, A. Gali, M. Toth, D. Englund and I. Aharonovich. "Bright Room-Temperature Single-Photon Emission from Defects in Gallium Nitride". Advanced Materials, 2017.

S. Fiedler, C. Ton-That and M. R. Phillips. "Enhanced UV emission of Au-coated nanorods via plasmon polariton-exciton coupling", E-MRS Fall 2016

S. Fiedler, C. Ton-That and M. R. Phillips. "Investigation of the optical properties of ZnO nanorods coated with Au nanoparticles", ICONN 2016

Contents

List of Figures

List of Tables

List of Abbreviations

ABX	Neutral **A**cceptor **B**ound e**X**citon
AFM	**A**tomic **F**orce **M**icroscopy
ALD	**A**tomic **L**ayer **D**eposition
ASF	**A**tomic **S**ensitivity **F**actor
BSE	**B**ack **S**cattered **E**lectrons
BX	**B**ound e**X**citon
CCD	**C**harge-**C**oupled **D**evice
CL	**C**athodo**L**uminescence
DBX	**D**onor **B**ound e**X**citon
DAP	**D**onor-**A**cceptor **P**air
DL	**D**eep **L**evel
EL	**E**lectro**L**uminescence
EQE	**E**xternal **Q**uantum **E**fficiency
FDTD	**F**inite-**D**ifference **T**ime-**D**omain
FWHM	**F**ull **W**idth at **H**alf **M**aximum
FX	**F**ree e**X**citon
GL	**G**reen **L**uminescence at 2.3 eV
GL$_1$	**G**reen **L**uminescence at 2.45 eV
HMT	**H**exa**M**ethylene**T**etramine
IQE	**I**nternal **Q**uantum **E**fficiency
LED	**L**ight **E**mitting **D**iode
LEE	**L**ight **E**xtraction **E**fficiency
LO	**L**ongitudinal **O**ptical
LSP	**L**ocalised **S**urface **P**lasmon
LSPR	**L**ocalised **S**urface **P**lasmon **R**esonance
MFP	**M**ean **F**ree **P**ath
MQW	**M**ultiple **Q**uantum **W**ell
NBE	**N**ear **B**and **E**dge
ND	**N**eutral **D**ensity
OL	**O**ange **L**uminescence
PL	**P**hoto**L**uminescence
RL	**R**ed **L**uminescence
sccm	**s**tandard **c**ubic **c**entimetres per **m**inute
SE	**S**econdary **E**lectrons
SER	**S**pontaneous **E**mission **R**ate
SEM	**S**canning **E**lectron **M**icroscopy
SPP	**S**urface **P**lasmon **P**olariton
SX	**S**urface e**X**citon
TES	**T**wo-**E**lectron **S**atellite

TE	**T**ransverse **E**lectric
TEM	**T**ransmission **E**lectron **M**icroscopy
TM	**T**ransverse **M**agnetic
TR-PL	**T**ime-**R**esolved **P**hoto**L**uminescence
UV	**U**ltra-**V**iolet
UV-Vis	**U**ltra-**V**iolet **Vis**ible
XPS	**X**-Ray **P**hotoelectron **S**pectroscopy